Modeling of the Creep Modulus of NOVA 2P for Predicting Creep at 20°C for 20 Years

Prepared for
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This report contains findings and results arrived at by theoretical analysis of material properties to describe product performance. It is not intended to constitute a recommendation for, or endorsement of, or certification of the product or its performance.

Summary

Argonne National Laboratory is considering the use of PVC for the construction of a detector array. Design information regarding the long-term creep behavior of the PVC compound is needed to determine the performance of extruded profile array-members for 20 years at 20°C.

An extruded profile sample, identified as NOVA 2P, was received 6/27/06.

Frequency-dependent flexural/tensile viscoelastic properties were obtained at various temperatures from 0 to 84°C. A specimen of the NOVA 2P profile was tested by starting at 84°C and incrementally decreasing temperature.

Frequency-Time-Superposition was used to construct master curves of the frequency-dependent viscoelastic properties of NOVA 2P at a reference temperature of 20°C. Temperature-dependence of the properties was defined by the FST α_T shift factor. A vertical shift factor, β_T, was required to produce the "best" constructed master curve.

Linear viscoelastic theory was used to convert the frequency-dependent loss and storage moduli data into loss and storage compliance data and then into time-dependent creep compliance data, the reciprocal of which is the "creep modulus". A performance prediction model was developed.

Strain-dependent viscoelastic property measurements reveal two "break-points" in the behavior of NOVA 2P. Linear viscoelastic behavior is confined to strains below 0.07%. A maximum in the loss tangent occurs at strains of approximately 0.3 to 0.4%, the second "break-point". Struik[5] has shown for PVC that as long as creep strains are maintained below 0.3 to 0.5%, creep behavior and the dynamics of aging are not affected by level of stress. These observations suggest that a "safe" ultimate/maximum strain of 0.5% could be used for design purposes. This translates to an applied creep stress of approximately 685 psi.

Sample

A piece of extruded PVC profile, identified as NOVA 2P, was received on 6/15/06.

Introduction

Argonne National Laboratory is considering the use of PVC for the construction of a detector array. Design information regarding the long-term creep behavior of the PVC compound is needed to determine the performance of extruded profile array-members for 20 years at 20°C. This report focuses on the use of “accelerated testing” and analysis of the resulting data to provide estimates of the long-term creep modulus of the NOVA 2P extruded profile. The experimental approach was to develop master curves of the frequency- and temperature-dependent viscoelastic properties. The frequency-dependent properties are then transformed, via linear viscoelastic (LVE) theory, to time-dependent creep compliance, the reciprocal of which is defined as the “creep modulus”.

Experimental

Test specimens were excised from regions of relatively uniform thickness within the extruded profile samples.

A Rheometrics RSAII solids analyzer, equipped with the dual-cantilever test fixture, was used to obtain the frequency-dependent flexural/tensile viscoelastic properties of the as-received PVC specimen over an angular frequency range of 100 to 0.0316 radians/s. The dynamic tensile strain amplitude was maintained “constant” at 0.02% for all test conditions. Testing was initiated at 84°C, using incrementally decreasing temperature (4 to 10°C, depending on proximity to the glass transition temperature) to a final temperature of 0°C. A minimum of 7 minutes was used for equilibration at each temperature prior to performing the frequency-dependent measurements. A dry nitrogen purge was used for testing at temperatures lower than 30°C; dry air was used at other temperatures.

Results and Discussion

The measured viscoelastic properties include the tensile storage modulus, E’, the loss modulus, E”, the complex modulus, |E*|, and the loss tangent, tan δ. The tensile storage modulus, E’, represents the elastic response component to the cyclic flexural deformation of the specimen. The tensile loss modulus, E”, represents the “viscous” response component. The complex tensile modulus, |E*|, is the vector sum of the E’ and E” response components. The loss tangent, tan δ, is equal to the ratio E”/E’ that describes the energy lost during cyclic deformation and readily reveals which of the two response components dominate behavior. Loss tangents less than 1 indicate an elastic-dominated behavior for a material that “remembers” its original shape. Loss tangent values greater than 1 indicate viscous-dominated behavior for a material that will tend to “flow” during a deformation and will tend to “forget” its original shape (for temperatures above the glass transition). Another feature of the loss tangent is that it displays a maximum at the glass transition temperature of the polymer. As will be shown, the NOVA 2P PVC specimen is elastic-dominated for all conditions that provide “structural” behavior.

Frequency-Temperature-Superposition (FTS) is a theoretical-based method [(1)] that allows one to combine sets of frequency-dependent properties obtained at various temperatures to produce master curves of the properties at a reference temperature that covers an extended range of frequencies. FTS is rigorously valid for temperatures near and above the glass transition temperature, but it is often conceptually extended to temperatures below the glass transition temperature as an empirical method for estimating behavior. The premise of FTS is that increasing test temperatures accelerate “molecular relaxation processes”. A process will require a shorter time for completion at a higher temperature than it will at a lower temperature. Additionally, FTS is valid only if the polymer maintains the same “state” at all testing conditions, e.g. the polymer can not undergo a change in molecular structure such as a melt transition or thermal degradation.

Viscoelastic Property Measurements and Master Curve Construction:

A previous report [2] provided a rationale and a rather detailed description of the methodology that was used to develop master curves of the viscoelastic properties of ANL PVC (1111-BB). A similar methodology is used within the present report. Thus, results will be provided using a “summary format”.

Figure 1 displays the constructed master curves for the viscoelastic properties of the NOVA 2P at a reference temperature of 20°C. Although there is some data scatter in the E” master curve at test conditions that produce low loss tangent properties (higher uncertainty of instrument resolution of E”), the resulting master curves appear to be adequate representations of the data. The accompanying temperature-dependent α_T and β_T shift factors are shown in Figure 2. Additionally, the shift factor data for the previously tested ANL PVC [2] are provided within the figure for comparison. As shown, the α_T of the NOVA 2P is similar to that of the ANL PVC at temperatures less than 60°C but at higher temperatures it becomes much smaller that that of the ANL PVC. Specifically, larger magnitudes of frequency-shifting are required for the data of NOVA 2P at temperatures higher than 60°C than were required for the previous ANL PVC sample.

The E’ and E” data of Figure 1 were piece-wise curve-fit to provide the data defined by the solid blue curves. The resulting E’ and E” data were converted to dynamic compliance data, D’ and D”, in accordance with LVE relationships [3]. The calculated dynamic compliance properties are shown in Figure 3. LVE theory provides both exact and approximate relationships for transforming frequency-dependent moduli and compliances to the time-dependent stress relaxation modulus and creep compliance, respectively [4]. The approximate transformations provide the more convenient method for the present case where discrete dynamic moduli and compliance data are available. Note: The FTS α_T is the same for both frequency-dependent properties and time-dependent properties.

Figure 4 displays the results of these transformations. Creep compliance is displayed in the form of its reciprocal or “creep modulus”, for convenience of presentation/comparison. Often the frequency-dependent complex modulus, |E*|, is assumed to be a good approximation of the time-dependent creep modulus where time is equated to the reciprocal of frequency, as is shown in the figure. It is noteworthy that all three properties are essentially equivalent for much of the time-scale, i.e. over the region that is significantly dominated by the elastic response. At long-times, the loss response component becomes a larger contributor to the total response, resulting in separation of the three moduli. The stress relaxation modulus undergoes a more rapid decrease in magnitude with increasing time than does the creep modulus. Thus, stress relaxation modulus measurements will produce larger strain estimates if taken as a “substitute” for creep measurements.

Figure 5 compares the creep moduli master curves of the NOVA 2P and the previously tested and reported ANL PVC. As shown, the modulus of the NOVA 2P tends to be approximately 10 to 20% lower than the modulus of ANL PVC for the relatively short-time region but both tend to converge at times approaching the 20-year prediction target. These differences in creep modulus are attributable to compositional differences of the two PVC compounds.

At the conclusion of testing, the geometry of the NOVA 2P test specimen was found to be slightly different than originally assigned, largely because of specimen shrinkage or recovery of strains introduced during profile extrusion. Most of the recovery occurs at the highest temperature of testing, i.e. the initial 84°C, thus affecting the accuracy of essentially all of the data. The specimen was remounted and tested at 30°C, using the corrected geometry for the property calculations. Figure 6 shows the comparison for properties obtained during the sequential incremented temperature testing and at the conclusion of testing. As shown, the shapes of the viscoelastic tensile moduli are essentially the same. A vertical shift of 1.081 (8.1% increase) for the "during test" data produces nearly exact superposition of the two sets of data. This shift factor was applied to the creep modulus data of Figure 4 to correct for geometry changes during testing to produce the creep modulus of NOVA 2P shown in Figure 7.

The time-dependent creep modulus of Figure 7 was adequately curve-fit by a polynomial of degree 8 to form the "model" that allows prediction of the creep modulus of NOVA 2P. The curve-fit coefficients for Equation 1 are provided in Table I.

$$f = \log(1/D) = \sum_{i=0}^{8} c_i (\log(t/\alpha_T))^i \qquad (1)$$
$$1/D = 10^f$$

where $1/D$ = Creep Modulus (Pa)
t/α_T = Reduced Time (s)
c_i = Curve-Fit Coefficients

The accompanying α_T and β_T shift factors were also curve-fit to least-squares polynomials, as shown by Equation 2 and 3. The coefficients are provided in Table II.

$$g = \log(\alpha_T) = \sum_{i=0}^{7} a_i T^i \qquad (2)$$
$$\alpha_T = 10^g$$

where a_i's are Curve-Fit Coefficients
T = Temperature (°C)

$$h = \log(\beta_T) = \sum_{i=0}^{7} b_i T^i \qquad (3)$$
$$\beta_T = 10^h$$

where b_i's are Curve-Fit Coefficients

These equations and coefficients have been incorporated into a spreadsheet that allows calculation of the creep modulus for NOVA 2P for any temperature and time, provided that the criteria $-3 < \log(t/\alpha_T) < 12.6$ is obeyed. The spreadsheet accompanies the electronic copy of this report to the requestor.

Strain Dependence:

Figure 8 displays the strain-dependent complex tensile modulus and loss tangent for as-received NOVA 2P at three temperatures with an angular frequency of 10 radians/s. These data display two regions of behavior. For dynamic strains less than 0.07%, the complex modulus remains constant and loss tangent slowly increases. These features can be considered indicative of linear viscoelastic behavior (although the rigorous definition is that all properties remain constant). If deformations remain within a 0.07% strain, then departure from LVE theory should be minimal which allows the confident use of the predictive model that was derived from “small strain” dynamic viscoelastic properties.

A second strain criterion is displayed as a peak in the loss tangent. The “peak” could not be completely resolved because of instrument limitations, but it appears to occur at a strain of approximately 0.3 or 0.4%. Struik [(5)] has shown for PVC that as long as creep strains are maintained below 0.3 to 0.5%, creep behavior and the dynamics of aging are not affected by level of stress. Based upon the occurrence of the peak in loss tangent, the modest reduction of approximately 10% in complex modulus at 0.4% strain and the findings of Struik, it is likely that confident use of the predictive model can be extended to maximum strains of 0.4 to 0.5

Table III contains estimates of applied loads for the various strain criteria for 20-year performance. Based on the creep modulus predictions of the model for NOVA 2P and a maximum strain of 0.5%, the applied creep stress is 685 psi.

Caveat:

The use of FTS to provide predictive performance models involves some degree of approximation. No guarantee is offered regarding the accuracy of the derived model(s) for predicting long-term creep performance.

References:

1. Ferry, John D., “Viscoelastic Properties of Polymers”, 2nd Ed., John Wiley & Sons, Inc., 1970, Chapter 11.

2. Harrell, E. Ray, “Modeling of the Creep Modulus of PVC 1111-BB for Predicting Creep at 20°C for 20 Years”, PolySciCon LLC Project # 028 to Jim Grudzinski, March 3, 2006.

3. Ferry, John D., “Viscoelastic Properties of Polymers”, 2nd Ed., John Wiley & Sons, Inc., 1970, p. 15.

4. Ferry, John D., “Viscoelastic Properties of Polymers”, 2nd Ed., John Wiley & Sons, Inc., 1970, Chapter 3 and 4.

5. Struik, L.C.E., "The Mechanical Enhancement of Physical Aging", *Polymer*, August 1980.

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Table I. Creep Modulus, 1/D(t), Polynomial Coefficients for NOVA 2P with Decreasing Temperature

c_0	9.588056553E+00
c_1	-1.134806280E-02
c_2	9.311505825E-04
c_3	-9.885827892E-04
c_4	-2.723038540E-05
c_5	5.118883876E-05
c_6	-6.660069999E-06
c_7	1.622890113E-08
c_8	1.623791982E-08

Table II. α_T and β_T Shift Factors Polynomial Coefficients for NOVA 2P with Decreasing Temperature

a_0	7.466381596E-01	b_0	-3.494028480E-02
a_1	7.120473381E-03	b_1	2.874384303E-03
a_2	-6.598684206E-03	b_2	-2.061045416E-04
a_3	4.165785481E-04	b_3	1.219358480E-05
a_4	-1.465352549E-05	b_4	-2.564252021E-07
a_5	2.867061626E-07	b_5	1.489283645E-09
a_6	-2.921443491E-09	b_6	1.261115399E-11
a_7	1.164812004E-11	b_7	-1.242936829E-13

Table III. Predicted Maximum Loads at 20°C for Various Estimated Creep Moduli and Critical Strain Criteria

Creep Modulus at 20 yrs (psi)	Critical Strain Criteria (%)			
	0.07	0.3	0.5	0.8
	Applied Stress (psi)			
136948	95.9	410.8	684.7	1095.6

Figure 1. Tensile Viscoelastic Properties of NOVA 2P PVC at 20°C

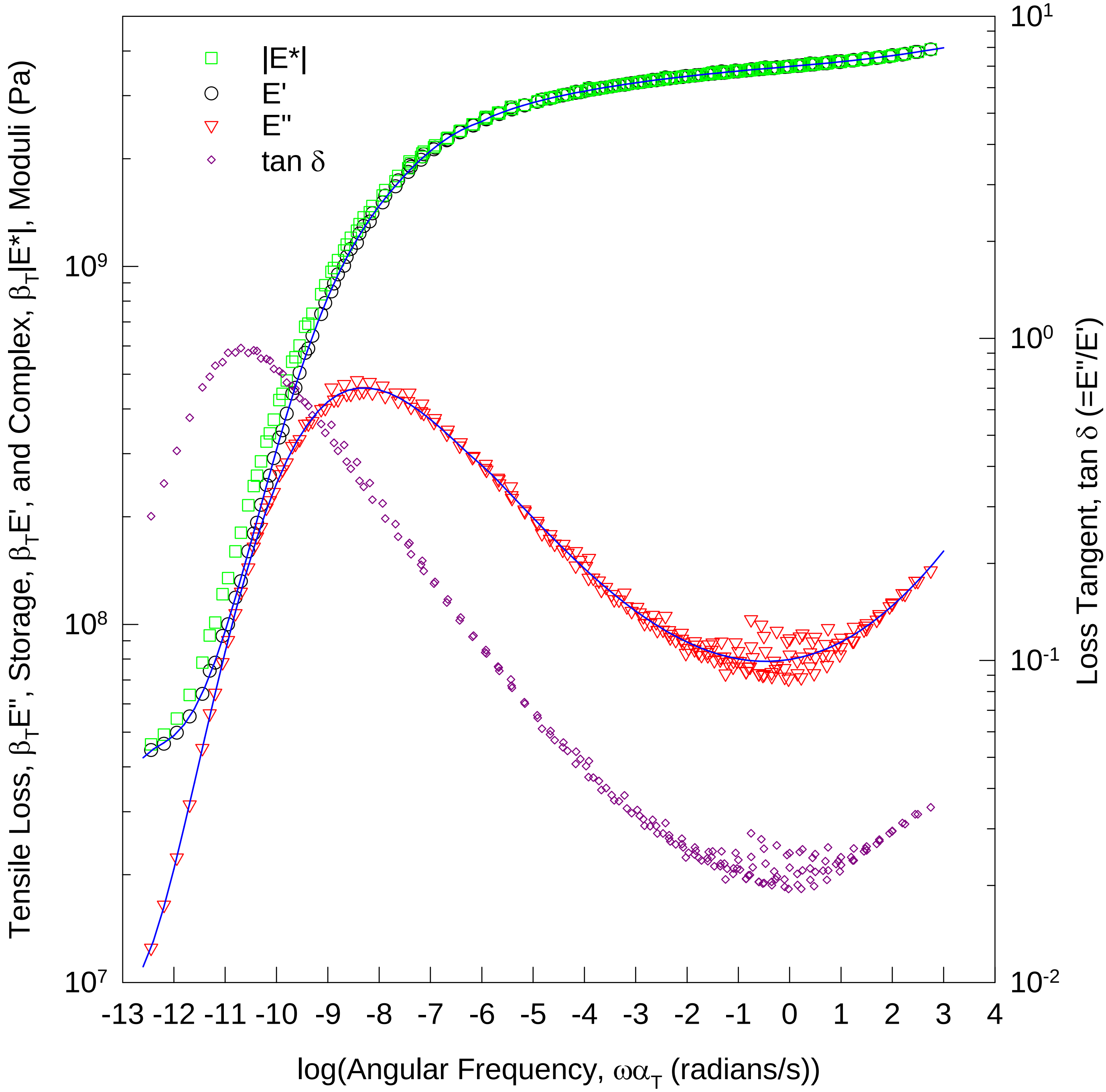

Figure 2. FTS Shift Factors, α_T & β_T, of NOVA 2P and ANL PVC for a Reference Temperature of 20°C

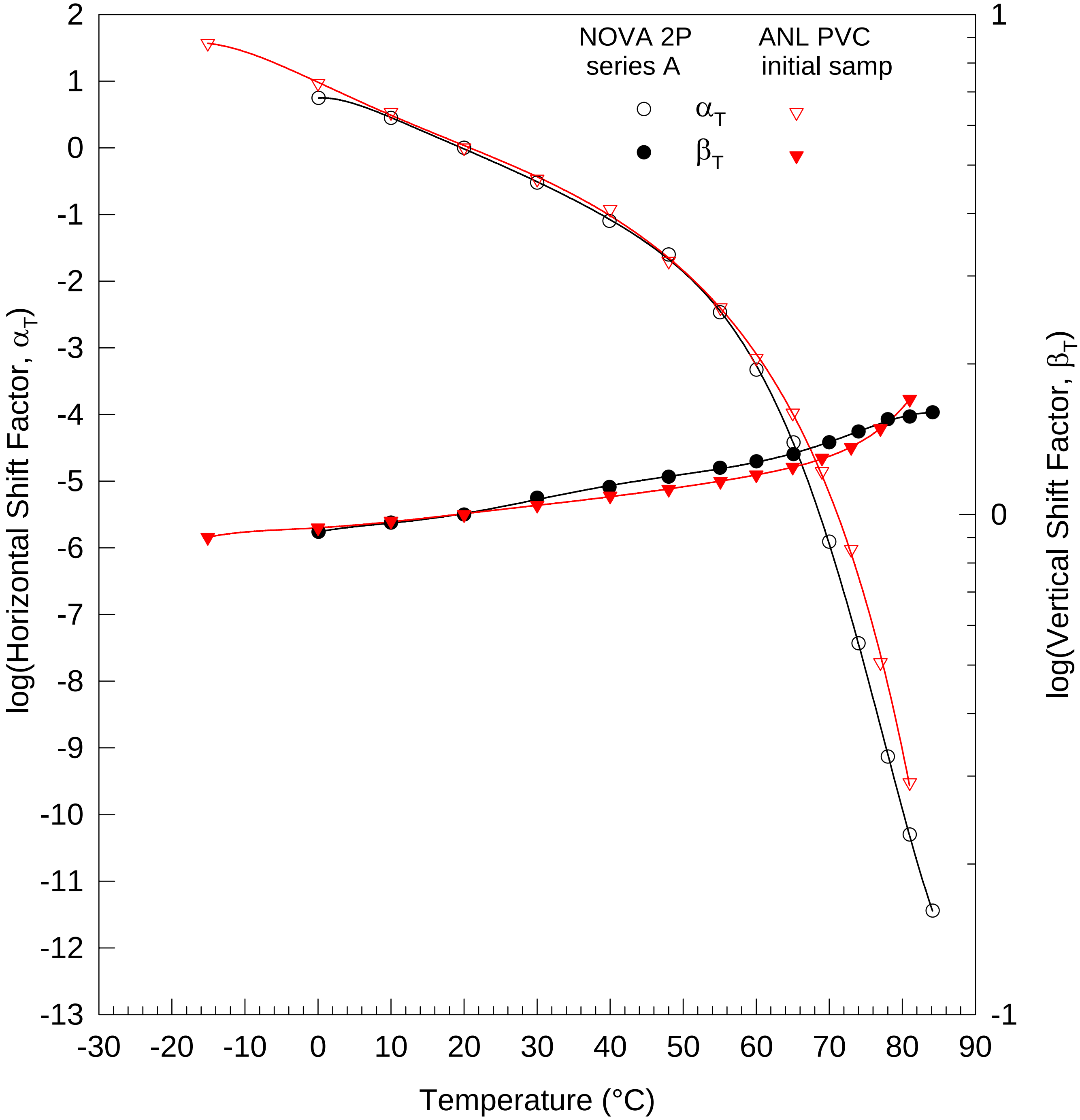

Figure 3. Tensile Dynamic Compliance Properties of NOVA 2P at 20°C

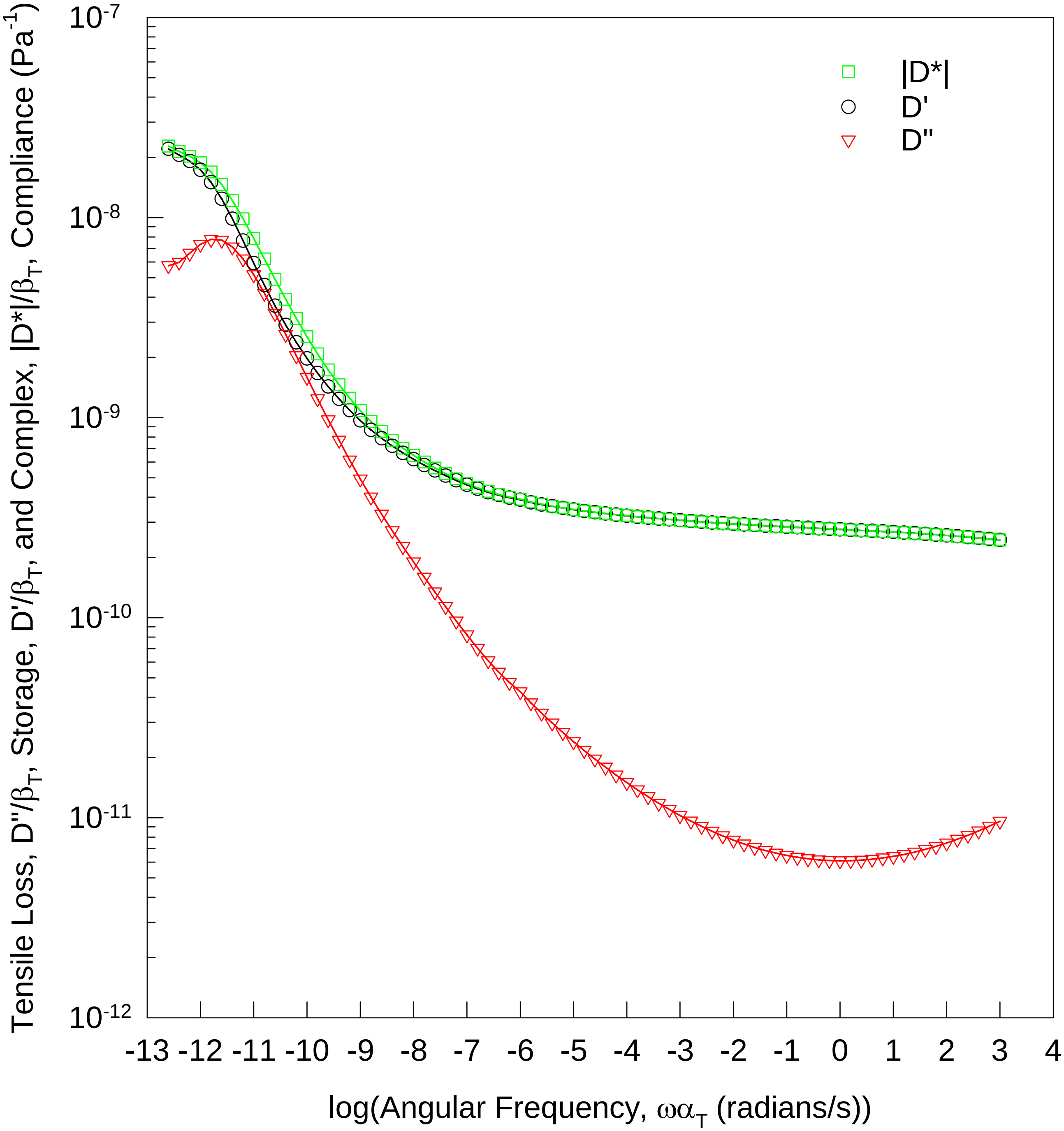

Figure 4. Calculated Tensile "Creep Modulus" of NOVA 2P PVC at 20°C

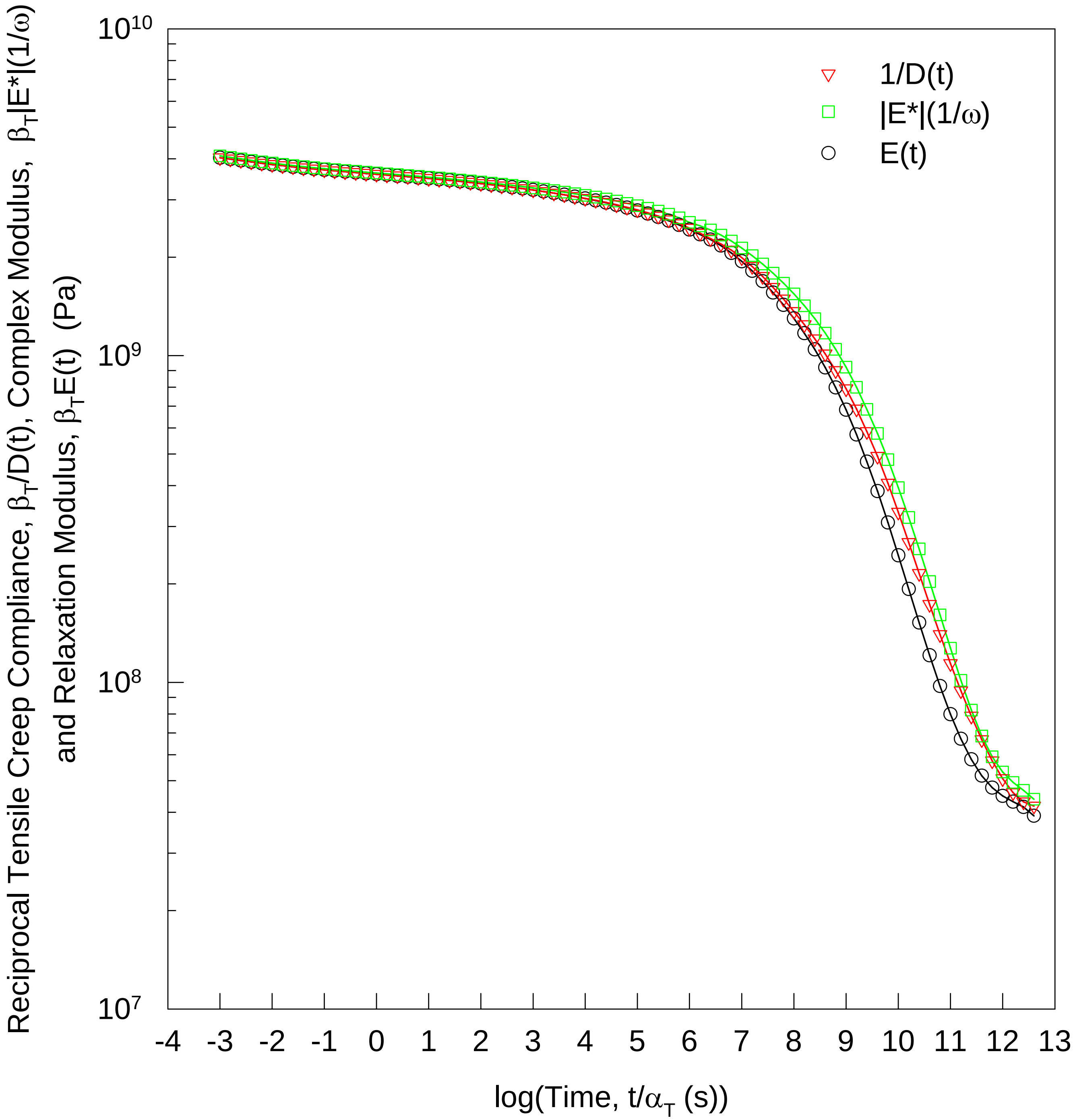

Figure 5. Comparison of Tensile "Creep Modulus" of NOVA 2P with ANL PVC (Initial Sample) at 20°C

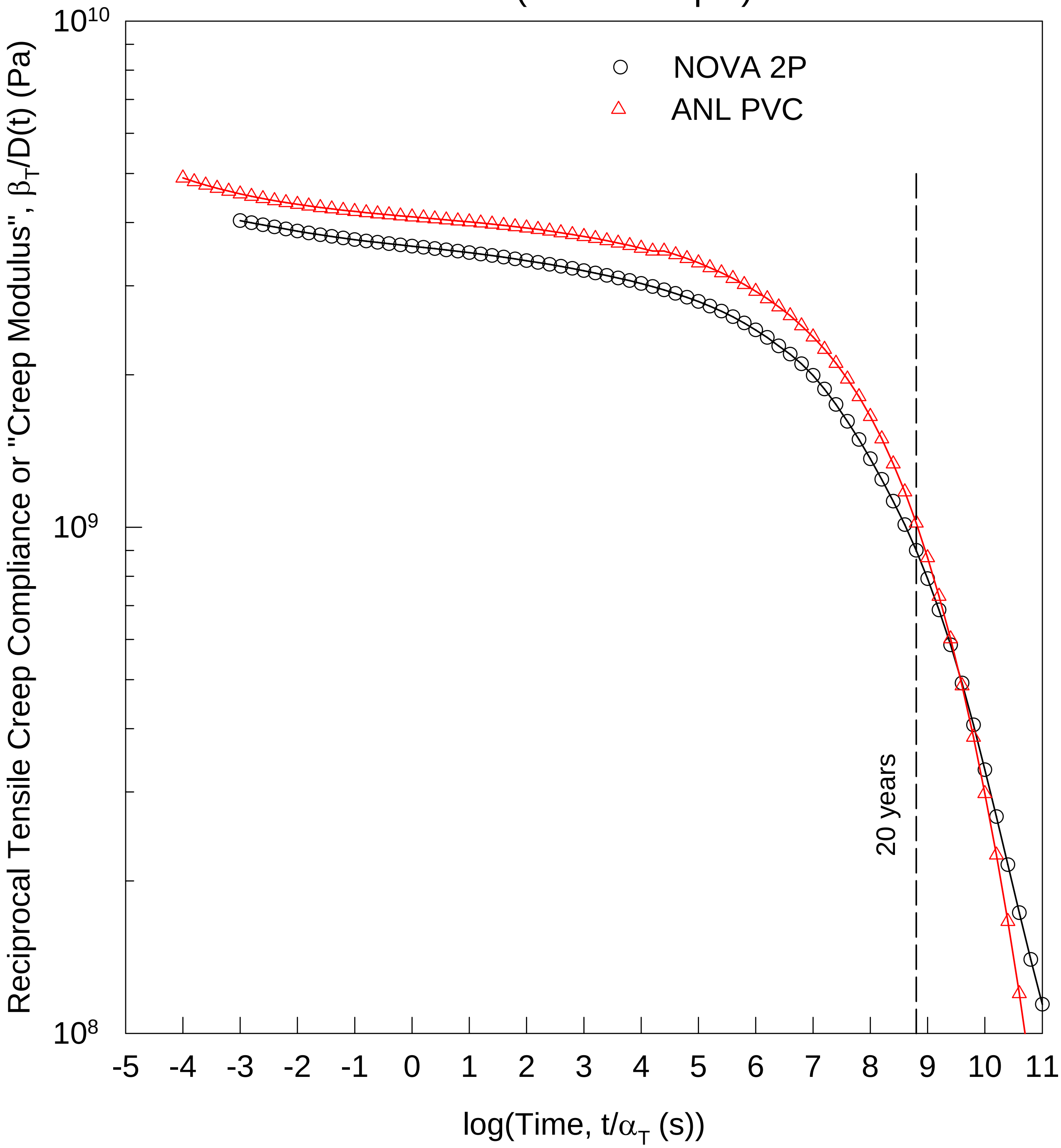

Figure 6. Tensile Viscoelastic Properties of NOVA 2P at 30°C, Measured During and After Testing

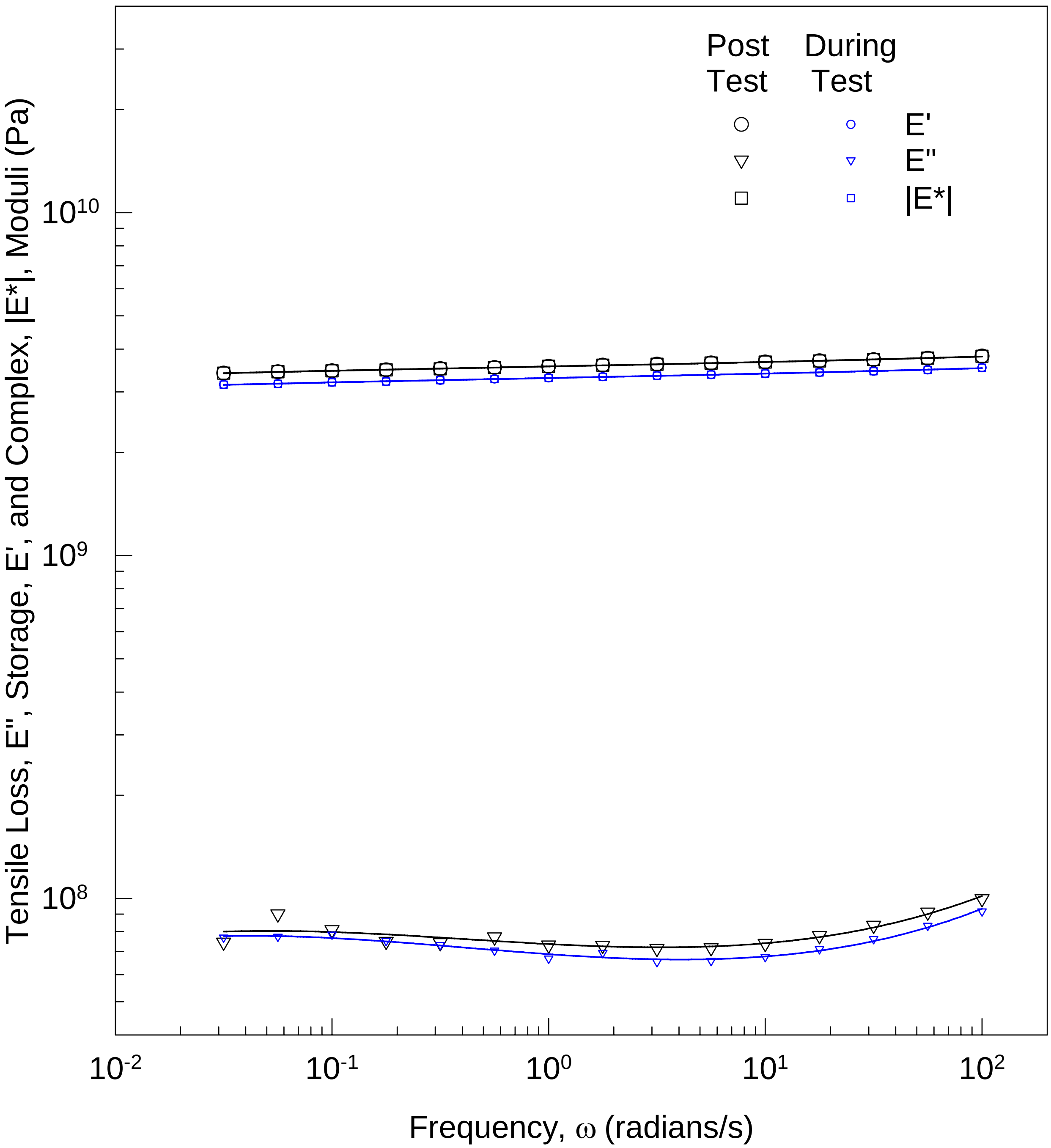

Figure 7. Curve-Fit of Calculated Tensile "Creep Modulus" of NOVA 2P PVC at 20°C

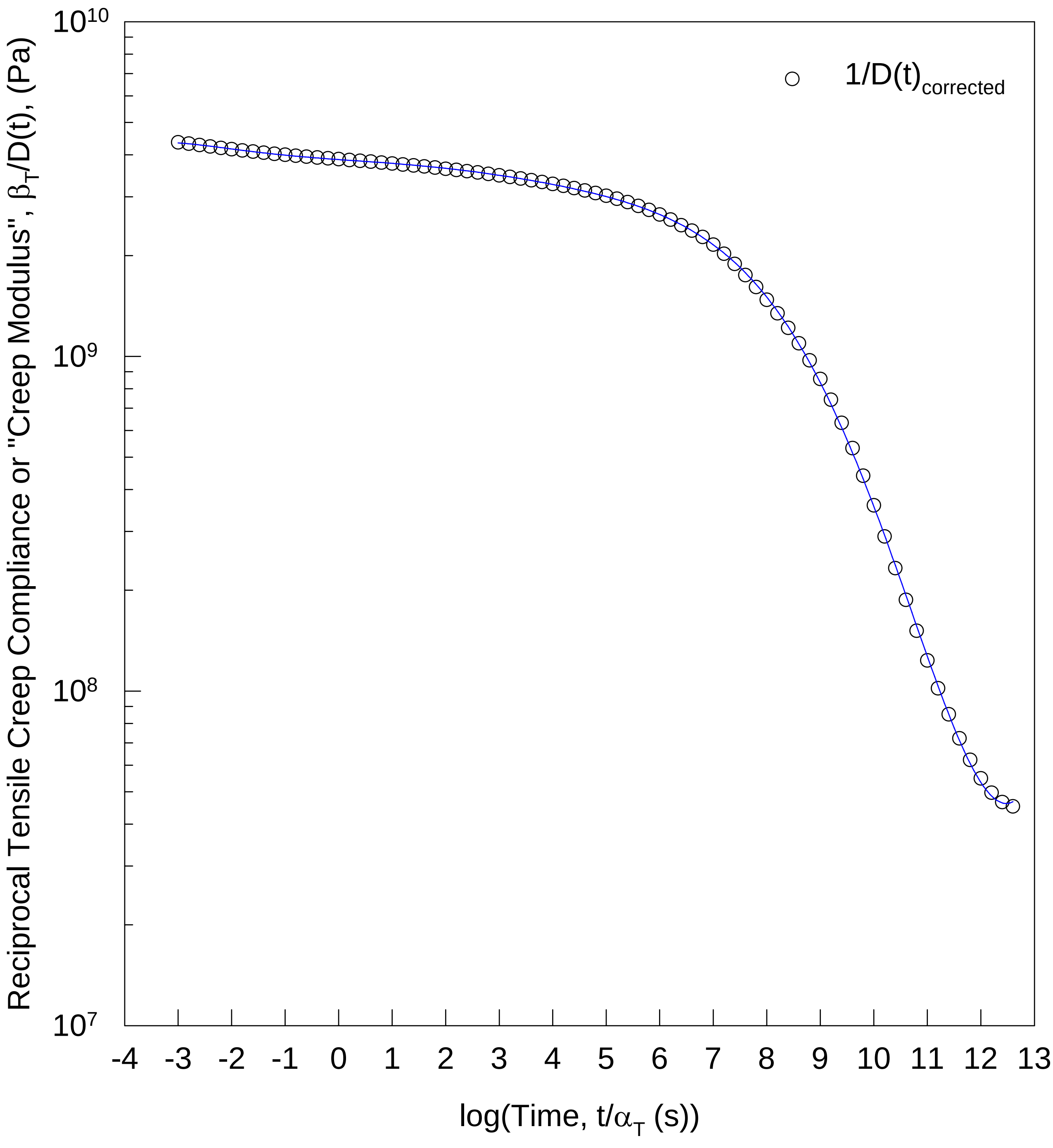

Figure 8. Strain-Dependent Properties of NOVA 2P at Various Temperaures; 10 rad/s